Technical Physics, 2024, Vol. 69, No. 8

06

Interfacial adhesion in the „MWCNT/Ti“ system and its improvement using ion beam treatment: a comparative analysis of the effects of argon and helium ions

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Received March 22, 2024
Revised May 17, 2024
Accepted May 31, 2024

A comparative study of the adhesion of multi-walled carbon nanotubes (MWCNTs) to a titanium surface, depending on the modes of irradiation with He^+ and Ar^+ ions of the „MWCNT/Ti“ system, was carried out using atomic force microscopy and X-ray photoelectron spectroscopy. A quantitative assessment of the adhesion force at the interface, performed using atomic force microscopy, demonstrated its significant increase as a result of the treatment of „MWCNT/Ti“ with high-energy helium and argon ions. This increase in adhesion force was found to depend on the time of ion irradiation and the type of ions. The nature of chemical bonding between MWCNTs and the surface of a titanium substrate, which causes an increase in the adhesion of nanotubes to titanium during ion irradiation, was studied using X-ray photoelectron spectroscopy. It has been established that this bonding is mainly the result of the formation of chemical C−O−Ti bonds between titanium and carbon atoms with the participation of oxygen atoms of oxygen-containing functional groups, which are localized on defects in the tube walls formed during ion irradiation. With long-term (30 min) irradiation with argon ions, weak effects of direct bonding between titanium and carbon atoms are observed in the photoelectron spectra, which also enhances interfacial adhesion.

Keywords: multi-walled carbon nanotubes (MWCNTs), irradiation with helium and argon ions, interfacial adhesion, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS).

DOI: 10.61011/TP.2024.08.59015.97-24

Introduction

The continuous miniaturization of various electronic devices is currently driving the active development of the industry of portable chemical power sources: lithium-ion batteries and supercapacitors [1,2]. Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), which have high conductivity, large specific surface area, and significant flexibility, are widely considered as the basis for the electrodes of such devices [3,4]. At the same time, the use of MWCNTs due to the variety of their shapes and configurations is estimated as more promising in comparison with SWCNTs. In addition, the process of separating MWCNTs from their bundles and subsequent dispersion is well understood and therefore less labor-intensive. However, the practical application of this class of materials is significantly complicated by the poor adhesion of MWCNTs to the conductive substrate. At the moment, the problem of low adhesion of the electrode material to the substrate is solved in production of the electrode by adding polymer binders: polyvinylidene fluoride (PVDF), carboxymethylcellulose (CMC), styrene butadiene latex (SBR), etc. [5–7]. However, this approach is accompanied by a significant decrease of the conductivity of the electrode material, which results in the need to search for new binder compositions, as well as other methods to increase the adhesion of the electrode material to the substrate.

The methods of irradiation with Ar^+ ions and microwave treatment of the interface were tested as alternative methods to increase the adhesion of the carbon layer to the substrate in Ref. [8,9] on the example of „MWCNT/Ti“ demonstrating the promising potential of such approaches to the problem of adhesion enhancement. These studies focused on the qualitative study of interfacial adhesion in „MWCNT/Ti“ without its quantitative evaluation, which significantly complicates the understanding of the nature of increasing the adhesive strength of MWCNTs on the surface of a titanium substrate.

According to [10–15], the adhesive strength of the carbon nanotube layer to the substrate can be quantified by macro and micromechanical experimental methods. The adhesive strength for these materials is determined by the applied force (shear, tensile, or peel) required to break the adhesive bond between both substrate and coating. Qualitative methods for evaluating adhesion in „carbon nanotubes—substrate“ systems do not provide reliable results, since they do not have a standardized procedure [9,16,17].

The prospects for using atomic force microscopy (AFM) to characterize the properties of the nanotubes were analyzed in Ref. [10,15,18–21]. The possibility of quantitative determination of the adhesive strength by AFM was demonstrated as a result of these studies, which in the future will allow for numerical comparison and control of the adhesive strength of carbon nanostructures to different substrates.

This work covers a complex experimental study of the initial „MWCNT/Ti“ systems and „MWCNT/Ti“ systems irradiated with $He^+(Ar^+)$ ions using AFM and X-ray photoelectron spectroscopy (XPS) methods, supplemented with data from scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA) to characterize the morphology of the studied objects. The main tasks of the work are: (i) comparative analysis of the results of quantitative AFM assessment of the strength of interfacial adhesion of MWCNTs to the titanium surface for various characteristics of the process of irradiation (type of ions used and treatment time) of the surface of the „MWCNT/Ti“ system; (ii) detection by XPS of differences in the increase of the adhesive strength when comparing the initial system and systems irradiated with $He^+(Ar^+)$ ions.

1. Experimental method

In this work, commercial MWCNTs (MWCNTs-2, produced by the G.K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences) [22] with a specific surface area of $250\,m^2/g$ and an outer diameter of nanotubes of 4–21 nm were used. A suspension was prepared at the first stage by dispersing the nanotubes in isopropyl alcohol for subsequent application of a layer of MWCNT on the surface of titanium foil. 5 mg of MWCNTs powder in 15 ml of alcohol were processed in Jeken Ultrasonic Cleaner (model PS-06A) for 5 h for this purpose. A layer of MWCNT was deposited on the titanium substrate ($\sim 50\,\mu m$ thick foil) heated to 70°C by spraying the suspension using an air compressor with a power of 10 W and a 10 L/min flow rate. The thickness of the obtained MWCNT layers was $\sim 1\,\mu m$.

Ion-beam treatment of the surface of „MWCNT/Ti“ system by ions of helium and argon with an average energy of 20 keV was carried out in a stationary mode using ion implanter „Composite“ for 10, 20 and 30 min. The ion beam was formed by ionization of helium and argon gas in a Penning discharge in crossed magnetic and electric fields. The average energy of the ion beam were chosen based on the planned thickness of the MWCNT film on Ti, which was calculated on the basis of the analysis of projective range of helium and argon ions in the MWCNT layer using program code SRIM-2013 [23]. The fluence of the beam and the degree of defectiveness of the MWCNT film on the substrate was varied depending on the duration of irradiation.

The morphology and element composition of the components of „MWCNT/Ti“ system before and after irradiation were studied by SEM and EDXA methods using electron microscope Jeol JSM 6610-LV with an energy dispersive spectrometer Inca-XAct.

The contact mode of the AFM method was used to quantify the adhesive strength of MWCNT layers to the titanium substrate and its changes as a result of the ion irradiation of „MWCNT/Ti“. The magnitude of the force (F) of application of the probe to the surface of the MWCNT layer necessary to separate the layer from the substrate with a gradual increase of the loading force from 0.3 to $40\,\mu N$ with a loading step of $0.2\,\mu N$ was determined for this purpose. The average value of the adhesive strength was calculated by measurement in ~ 100 different areas on the sample surface, located not less than $15-30\,\mu m$ from each other. Measurements were carried out using atomic-force microscope MFP-3D (Asylum Research) and cantilevers HA_HR (TipsNano) with a force constant of $k \sim 34$ N/m.

The examination of the nature of increase of the adhesion of MWCNT layers to titanium as a result of ion irradiation of „MWCNT/Ti“ and detailed characterization of the mechanism of this phenomenon was made on the basis of the results of the analysis of the shape of the C $1s$, O $1s$, and Ti $2p$ core-level photoelectron (CL PE) spectra and binding energies of their components for the initial and the irradiated „MWCNT/Ti“ systems. The measured PE spectra were used for obtaining additional information about the element composition of the studied systems. All measurements were carried out using a laboratory electron spectrometer ESCAlab 250 Xi and monochromatized AlK_α-radiation ($h\nu = 1486.6$ eV). The survey and CL (C $1s$, O $1s$, and Ti $2p$) PE spectra were recorded with the analyzer pass energy of 50, and 20 eV, respectively. The binding energy scale was calibrated using a pure gold foil for which the energy position of Au $4f_{7/2}$ PE line and the Fermi level was determined. The detailed analysis of the PE spectra was performed using the approximation of spectra of a set of individual components, using program code Casa XPS 2.3.16 [24].

2. Results and discussion

2.1. SEM

Figure 1 shows SEM images of a titanium substrate before and after deposition of the MWCNT layer on it. The comparison of SEM images in Fig. 1 allows concluding that a continuous layer of MWCNT is formed on the surface of a titanium substrate with an average external diameter of nanotubes up to 20 nm. Nanotubes in the layer are located

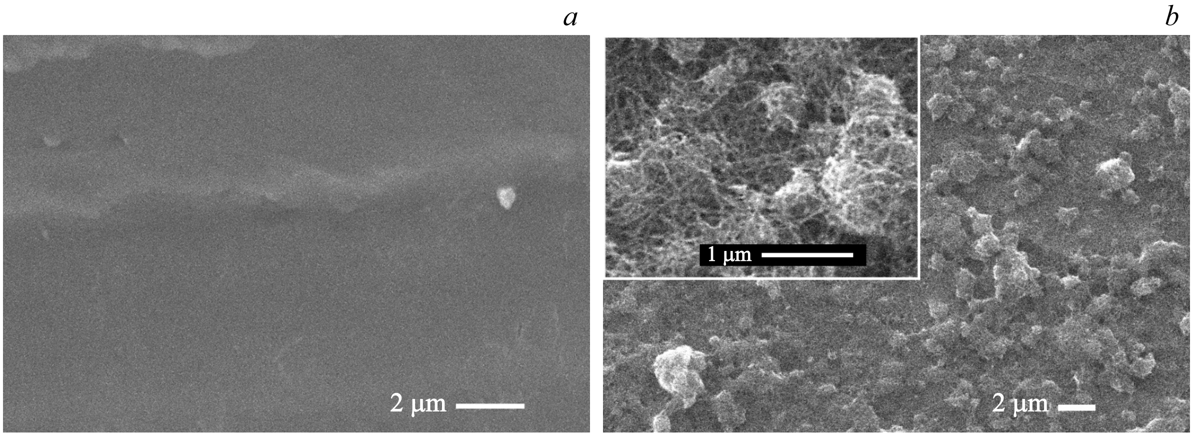

Figure 1. SEM images of the Ti substrate surface (*a*) and the surface layer of „MWCNT/Ti“ system (*b*) before irradiation.

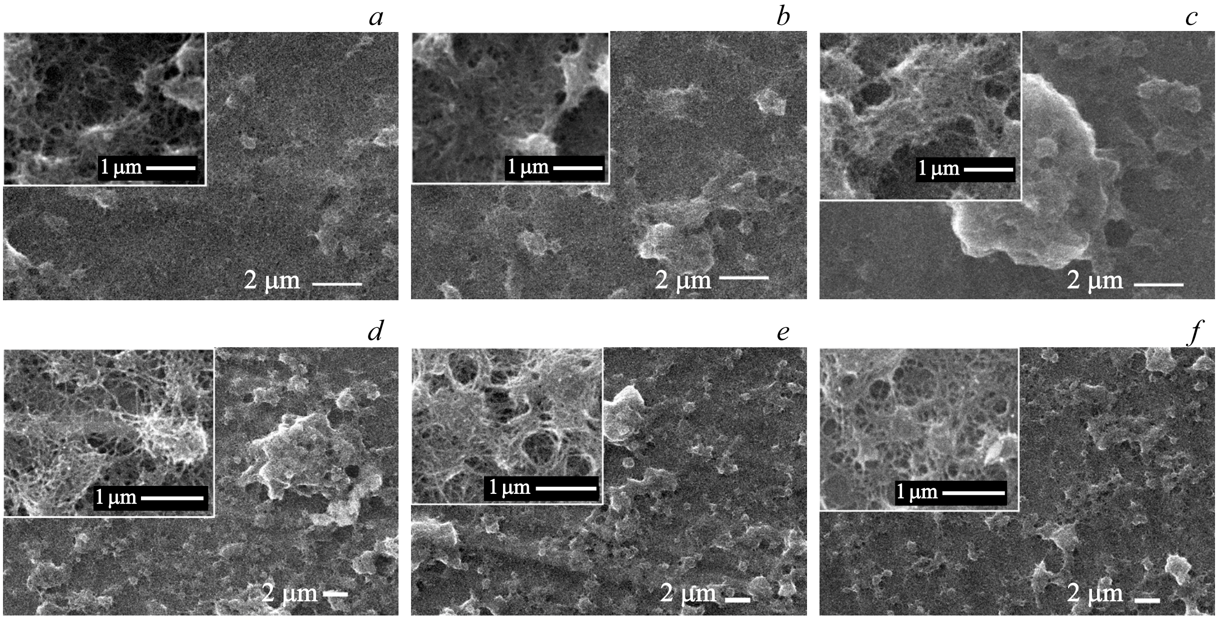

Figure 2. SEM images of the surface layer of „MWCNT/Ti“ system after 10 (*a*), 20 (*b*) and 30 min (*c*) irradiation with helium ions and after 10 (*d*), 20 (*e*) and 30 min (*f*) of irradiation with of argon ions.

mainly parallel to the substrate forming a set of intersections and overlap each other. Separate MWCNTs agglomerates with the size of $1-2\,\mu$m not having any clear boundaries formed during the deposition of the layer are observed on the layer surface.

The irradiation of the MWCNT layer on a titanium substrate with helium and argon ions was carried out with different exposure time (Fig. 2). The formation of clearer agglomerate boundaries on the layer surface is observed in the result of 10 min irradiation due to round-shaped voids (Fig. 2, *a, d*), the formation of which is probably associated with partial destruction of nanotubes under the impact of high-energy ions. In this case there are practically no special differences between the type of ions used (helium or argon) for a given irradiation time. The number of voids between nanotubes and their sizes increase to $\sim 500-800$ nm with the increase of the irradiation time for both types of ions used (Fig. 2, *b, c, e, f*). The magnified SEM images of the MWCNT layer show evidence of MWCNTs welding with each other (insets in Fig. 2, *b, c, e, f*). Moreover, in the case of argon ions, these changes are expressed stronger, which can be attributed to the higher mass of this type of ions compared to helium ions and, as a consequence, the formation of predominantly extended structural defects in the MWCNT walls. Thus, the irradiation with a beam of helium and argon ions results in the observed pronounced morphological changes in the MWCNT surface layers.

2.2. EDXA

The element analysis data obtained by the EDXA method with averaging over several points for each sample are

Table 1. Quantitative elemental composition according to EDXA data for the „MWCNT/Ti" system before and after irradiation with helium and argon ions

Sample	Concentration, at.%					
	He^+			Ar^+		
	[C]	[O]	[Ti]	[C]	[O]	[Ti]
MWCNT/Ti before irradiation	40.8	5.3	54.0	40.8	5.3	54.0
MWCNT/Ti, 10 min irradiation	35.7	4.2	60.1	37.1	3.6	59.3
MWCNT/Ti, 20 min irradiation	29.7	7.4	62.9	31.6	5.5	62.9
MWCNT/Ti, 30 min irradiation	25.7	5.4	68.9	20.9	7.4	71.7

shown in Table 1. It is clearly seen that an increase of the titanium concentration and decrease of the carbon dioxide concentration is observed in the examined region of the samples with the increase of the time of ion-beam treatment of the MWCNTs surface for both types of ions used. This result is probably attributable to a decrease of the thickness and density of the MWCNT layer during the ion irradiation.

2.3. AFM

The interfacial adhesion of the MWCNT surface layer to the titanium substrate was quantified by the contact mode AFM method. The surface of the MWCNT layer was scanned at a speed of $50\,\mu$m/s and with an application force in the range of $0.3-40\,\mu$N, which increased in increments of $0.2\,\mu$N for each subsequent scanning. In this case, the discontinuity of the MWCNT layer on the titanium substrate was visually assessed by the reflection of light from the Ti surface using an integrated optical camera with a magnification of ×400. The adhesive strength (F, [μN]) was determined by the signal of the laser-optical console system (DFL, [V]) as $F = k\Delta z DFL$, where k is the spring constant of the cantilever, and Δz is the angle of the force−distance experimental curve, [nm/V].

The treatment with helium ions for 10 min does not result in a change of the value F as can be seen in Fig. 3, *a–d*, whereas an increase of the adhesive strength is observed after 20 and 30 min of irradiation. An increase of the value of the adhesive strength is observed relative to the initial „MWCNT/Ti" system when argon ions are used for all irradiation modes (Fig. 3, *e–g*). However, it should be noted that the maximum value of F is detected for 10 min in case of irradiation with argon ions and equals to $31.8\,\mu$N, while this parameter has a maximum value of $18.3\,\mu$N for 20 min in case of use of helium ions. Thus, it is obvious that both parameters (ion mass and irradiation time) affect the value of the adhesive strength. In this case, the duration of ion treatment in general affects the concentration of defects formed in the „MWCNT/Ti" system during its irradiation with high-energy ions, while the type (mass) of the ion affects the nature of the structural defects formed (point-like or extended). Consequently, an increase of the treatment time in case of usage of helium ions contributes to an increase of the concentration of mainly point-like structural defects at the „MWCNT/Ti" interface and, apparently, has a positive effect on the adhesive strength of the MWCNT layer to the titanium substrate. This effect is already observed after 10 min of treatment in the case of argon ion irradiation due to the formation of extended structural defects at the „MWCNT/Ti" interface.

2.4. XPS

Detailed analysis of CL C 1s, O 1s, and Ti 2p PE spectra of the „MWCNT/Ti" systems measured before and after irradiation with a beam of helium and argon ions provide the most complete information about the nature of the increase of the interfacial adhesion in these systems as a result of irradiation. Since the XPS method is surface sensitive and examines the sample only to a depth of the order of $3-5$ nm in the conditions of our experiment, all PE measurements were carried out in areas on the sample surface that contained a signal from a titanium substrate in addition to the signal from carbon and oxygen, which made it possible to study the „MWCNT/Ti" interface.

Figure 4 shows C 1s PE spectra of „MWCNT/Ti" before and after ion treatment. There are five components in the sample spectrum before irradiation (Fig. 4, *a*) that correspond to the graphite-like sp^2-carbon C=C ($\sim$ 284.6 eV, C1), sp^3-carbon C−C in diamond and/or carbon located near functional oxygen-containing groups [C*−C(O)] ($\sim$ 285.5 eV, C2), carbon in groups C−O ($\sim$ 286.4 eV, C3) and C=O ($\sim$ 287.5 eV, C4), as well as carbon in COOH groups ($\sim$ 289 eV, C5) [25–27]. High-energy maximum sh ($\sim$ 291 eV) is a satellite that is typical of the XPS spectra of sp^2-carbon atoms in systems with a high degree of graphitization and is associated with $\pi \to \pi^*$ *shake-up* a process that occurs simultaneously with C 1s photoionization [25].

Figure 4 clearly shows that the irradiation results in a significant changes in the shape of the C 1s PE spectra: increase of its width at half maximum (FWHM) from 0.7 to 1.45 eV (for He^+ ions) and from 0.7 to 1.71 eV (for Ar^+ ions), the redistribution of relative intensities of its components, and the disappearance of the *shake-up* satellite. All this indicates a change of the number of carbon atoms in different chemical states in the system, possible formation of additional chemical bonds between carbon atoms of MWCNTs and other atoms of the system, as well as significant defect formation in graphite-like walls of nanotubes. A detailed comparison of these spectra (Fig. 4, *b–d*) shows that the change of the FWHM for the C 1s spectra of irradiated MWCNT/Ti is attributable to the redistribution of the relative intensities of the C1 component (sp^2-carbon) and the C2, C3, C4, and C5 components, which pertain to carbon atoms interacting with oxygen atoms. These changes in the C 1s PE spectra of the irradiated systems indicate that the outer walls of MWCNTs

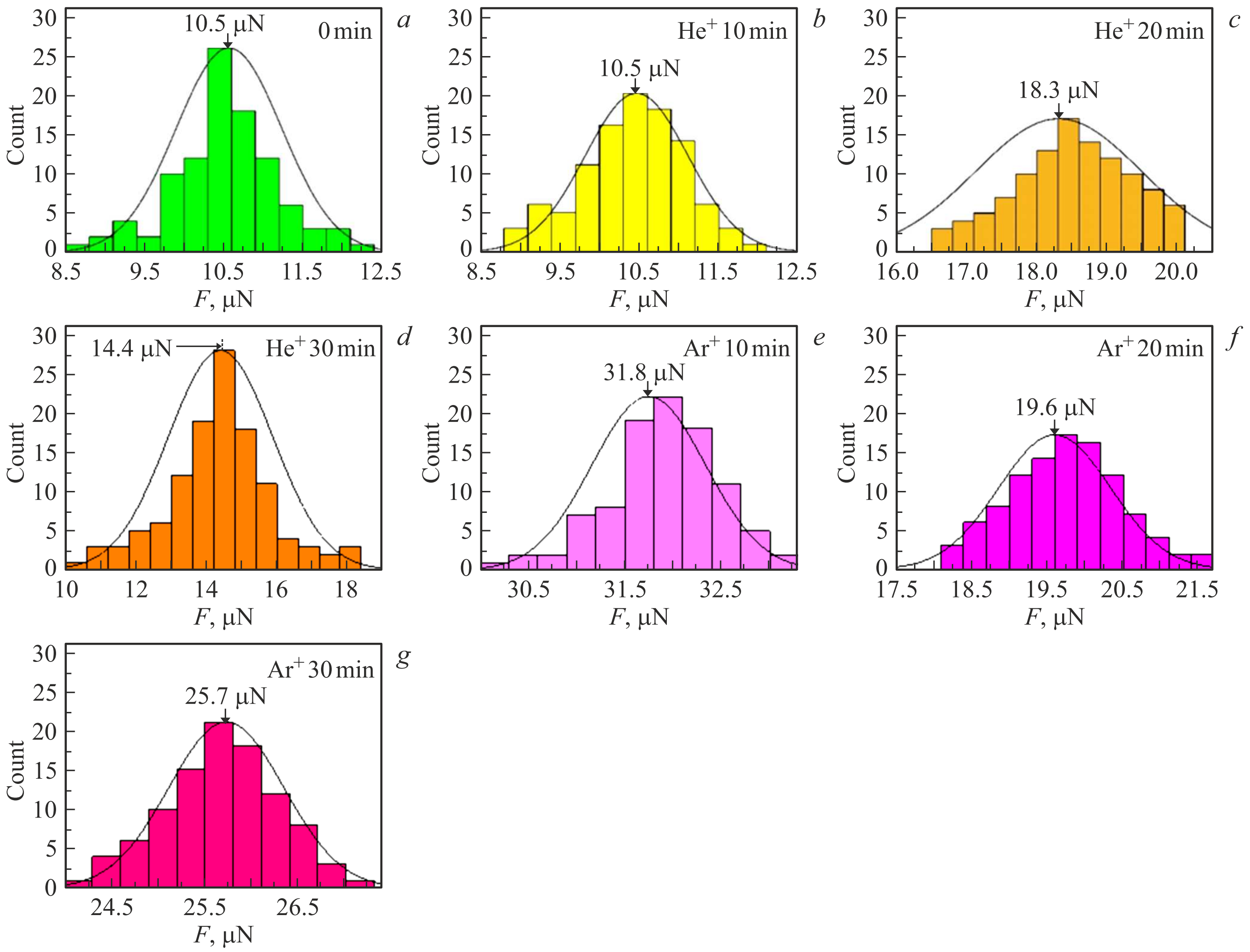

Figure 3. Histograms of the distribution of values of the adhesive strength of the MWCNT layer to the titanium substrate (a) before and after irradiation of the „MWCNT/Ti“ system with helium and argon ions for 10 (b, e), 20 (c, f) and 30 min (d, g).

undergo significant structural damage as a result of ion irradiation, which leads to an increase in the degree of wall defects and the attachment of oxygen-containing functional groups in the areas of formed defects. At the same time, an increase of the time of ion beam irradiation from 10 to 30 min for both types of used ions is accompanied by an intensification of the formation of structural defects and oxidation of the outer walls of MWCNTs. It is important to note that all C 1s PE spectra of samples irradiated with helium ions do not have a component corresponding to the binding energy of C 1s electrons in titanium carbide at the binding energy ~ 282.2 eV [28]. This component, denoted C0 on Fig. 4, d appears in the C 1s PE spectrum of the sample after 30 min exposure in the case of irradiation of MWCNT/Ti with argon ions, which indicates the possibility of formation of direct C–Ti-bonds between the MWCNTs and the Ti substrate.

Figure 5 shows Ti 2$p_{1/2,3/2}$ PE spectra of „MWCNT/Ti“ system measured before and after ion treatment. Next, we consider only the most intensive Ti 2$p_{3/2}$ spectrum. Three components corresponding to metallic titanium (~ 454.2 eV, Ti1) and oxidized states of titanium TiO_{1-x} and Ti_{2-x} (~ 456.4 eV, Ti2), as well as TiO_2 (~ 458.4 eV, Ti3) are observed in this spectrum of „MWCNT/Ti“ system before and after irradiation [29–31]. It should be noted that PE lines of oxides TiO_{1-x} and TiO_{2-x} in our previous study [8] were considered as separate components, however they were combined into a single component in the present work due to the complexity of approximation.

It is obvious from these data that oxide compounds of titanium atoms with different degree of oxidation maintaining a certain percentage of Ti^0 atoms prevail on the surface of titanium substrate in all samples. A decrease of the relative intensity of „metallic“ component Ti1 and an increase of the intensity of „dioxide“ component Ti3 are observed in the considered spectra of the samples with the increase of the irradiation time. Such changes may be related to further oxidation of titanium atoms in the process of ion-beam treatment. It should be emphasized

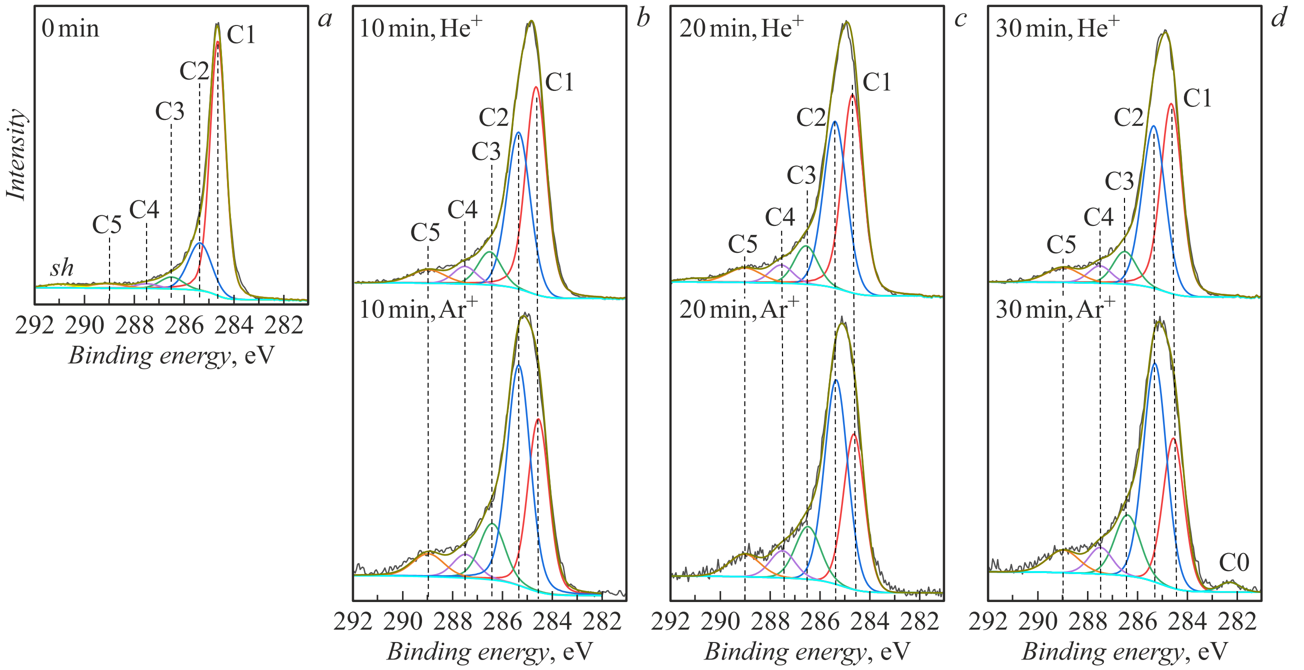

Figure 4. C 1*s* PE spectra of the surface layer of „MWCNT/Ti“ samples: before irradiation (*a*) and after 10 (*b*), 20 (*c*) and 30 min (*d*) irradiation with helium and argon ions.

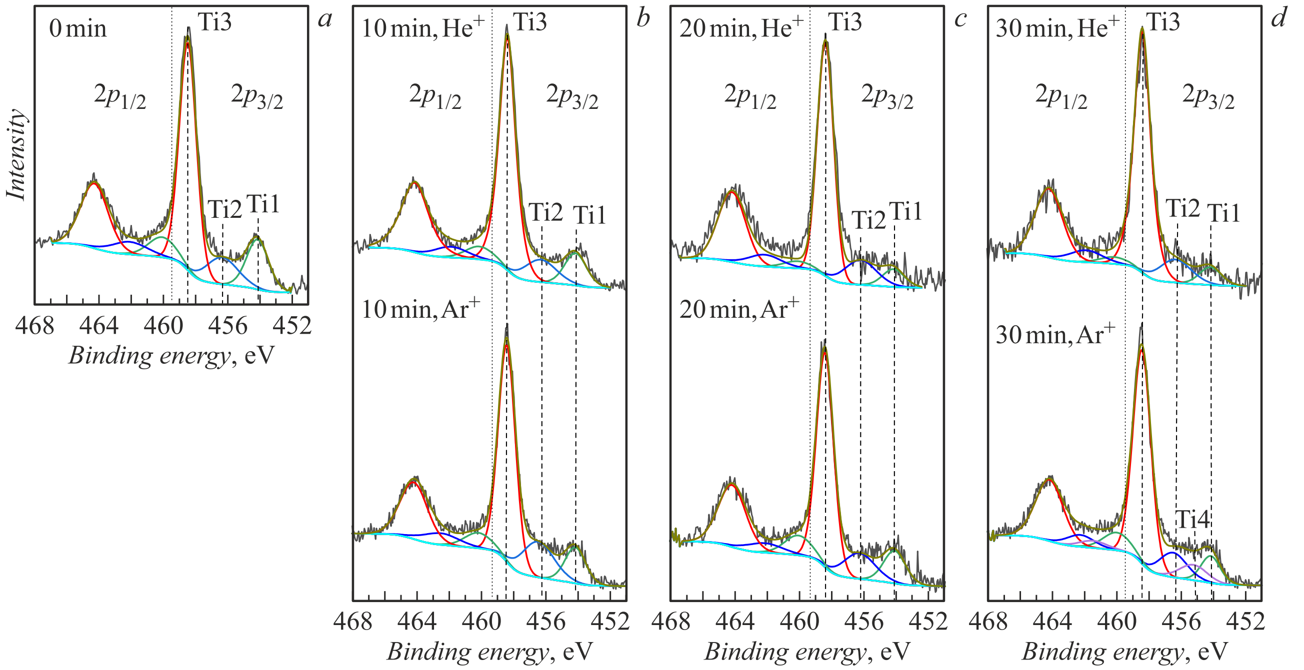

Figure 5. Ti $2p_{1/2,3/2}$ PE spectra of the surface layer of „MWCNT/Ti“ samples: before irradiation (*a*) and after 10 (*b*), 20 (*c*) and 30 min (*d*) irradiation with helium and argon ions.

that there are no components with the binding energy of ~ 455.4 and ~ 282.1 eV, respectively, associated with Ti and C atoms in the titanium carbides in Ti $2p_{3/2}$ and C 1*s* PE spectra of the samples irradiated with helium (10, 20, 30 min) and argon (10 and 20 min) ions [28]. This observation suggests that there is no direct chemical bonding between carbon and titanium atoms in these „MWCNT/Ti“ systems. Consequently, the observed increase of adhesion in case of irradiation of „MWCNT/Ti“ with helium and argon ions, cannot occur in the above modes due to the formation of chemical bonds between the atoms of titanium substrate and the carbon atoms in the MWCNT layer. The

Table 2. Results of a three-component approximation of the intensity distribution in O 1*s* PE spectra and estimates of the concentrations of various oxygen-containing components for the „MWCNT/Ti" system before and after irradiation

Sample	Relative component intensity, %			Concentration, at.%			
	O1	O2	O3	O_{tot}	O1	O2	O3
MWCNT/Ti before irradiation	70.4	24.5	5.1	26.12	18.36	6.43	1.33
MWCNT/Ti, 10 min irradiation He^+	42.7	43.3	14.0	20.65	8.82	8.94	2.89
MWCNT/Ti, 20 min irradiation He^+	35.3	43.3	21.4	18.74	6.62	8.11	4.01
MWCNT/Ti, 30 min irradiation He^+	29.4	49.7	20.9	16.45	4.83	8.17	3.45
MWCNT/Ti, 10 min irradiation Ar^+	48.4	32.0	19.6	23.99	11.61	7.67	4.71
MWCNT/Ti, 20 min irradiation Ar^+	51.0	29.3	19.7	22.03	11.23	6.45	4.35
MWCNT/Ti, 30 min irradiation Ar^+	59.0	25.7	15.3	27.02	15.95	6.94	4.13

only exception is the sample irradiated by argon ions during 30 min. For it, a Ti4 component is observed in the Ti $2p_{3/2}$ spectrum in the region of binding energies of 455−457 eV, characteristic of the energies of Ti $2p_{3/2}$ level in titanium carbides. It is likely that this observation reflects the presence of direct chemical bonding between carbon and titanium atoms in the studied system (Fig. 5, *d*). This is probably the reason why the value of the interfacial adhesive strength for this mode of irradiation with Ar^+ ions slightly is higher than in case of irradiation for 20 min (Fig. 3, *f*, *g*).

There are three components in the O 1*s* PE spectrum of the non-irradiated „MWCNT/Ti" system (Fig. 6, *a*) that correspond to the oxygen atoms in TiO_2 (∼ 530.6 eV, O1), as well as in oxygen-containing carbon groups with double and single chemical bonds between carbon and oxygen atoms: C=O (∼ 532.1 eV, O2) and C−O (∼ 533.1 eV, O3) [29,30]. The results of a three-component approximation of the O 1*s* PE spectra for the „MWCNT/Ti" system before and after irradiation are presented in Table 2.

The irradiation with helium ions of MWCNTs on a titanium substrate for 10 min results in a change of the shape and broadening of the O 1*s* PE spectrum. Both effects are attributable to an increase of the intensities of the O2 and O3 components, which correspond to the oxygen in the compounds of carbon with single and double chemical bond. A further increase of the relative intensities of the O2 and O3 components is observed after 20 and 30 min of treatment of „MWCNT/Ti" by an ion beam. The shape of O 1*s* PE spectra in the case of irradiation of „MWCNT/Ti" by argon ions is somewhat different from the shape of the spectra of the samples treated by He^+ ions, due to the lower relative intensity of the component O2. This result apparently indicates that much less chemical double C=O bonds are formed in the process of irradiation by Ar^+ ions. At the same time the O 1*s* PE spectra of the samples after 10 and 20 min of treatment by argon ions practically do not differ, whereas an apparent decrease of the relative intensity of the components O2 and O3 is observed in the spectrum of the sample after 30 min (Table 2). An ion-induced formation and destruction of C−O-groups localized at structural defects on the surface of carbon nanotubes, the number of which increases with the increase of the irradiation time can be a possible reason for the non-monotonic change of the relative intensity of O2 and O3. The change of the number of these C−O-groups was observed earlier in C 1*s* PE spectra of irradiated samples (Fig. 4).

By now it is known that a chemical bonding occurs between carbon nanomaterial (graphene or MWCNTs) and metal-oxide particles TiO_x, SnO_x or CuO deposited on the surface of the carbon nanomaterial in the process of preparation of composites based on this carbon nanomaterial [26,32–37]. This phenomenon is caused by the formation of direct chemical C−M [35–37] bonds or C−O−M-bonds resulting from the addition of metal atoms M to the C−O groups that appear on the surface of a carbon material at structural defects as a result of ion bombardment in an oxygen-containing atmosphere [8,26]. In our case, a combined analysis of C 1*s* and Ti 2*p* PE spectra showed that direct C−Ti bonds are formed only after 30 min irradiation with argon ions, and they are not formed in other modes. Therefore, the formation of C−O−Ti-chemical bonds is more likely for the modes of treatment with helium (10, 20, 30 min) and argon ions (10 and 20 min). At the same time, the energy position of the component corresponding to these bonds in the O 1*s* PE spectrum coincides with the position of the O2 component corresponding to the O 1*s* PE line of C=O-groups on the surface of the carbon material, which significantly complicates the interpretation of the experimental spectra [32]. Therefore, let us use the information about the content of C−O-groups obtained by including the share of component O3 relative to the total oxygen content determined from the survey spectrum (these spectra are not shown), for a specific sample (Table 2). It is clearly seen (Table 2) that its concentration considerably

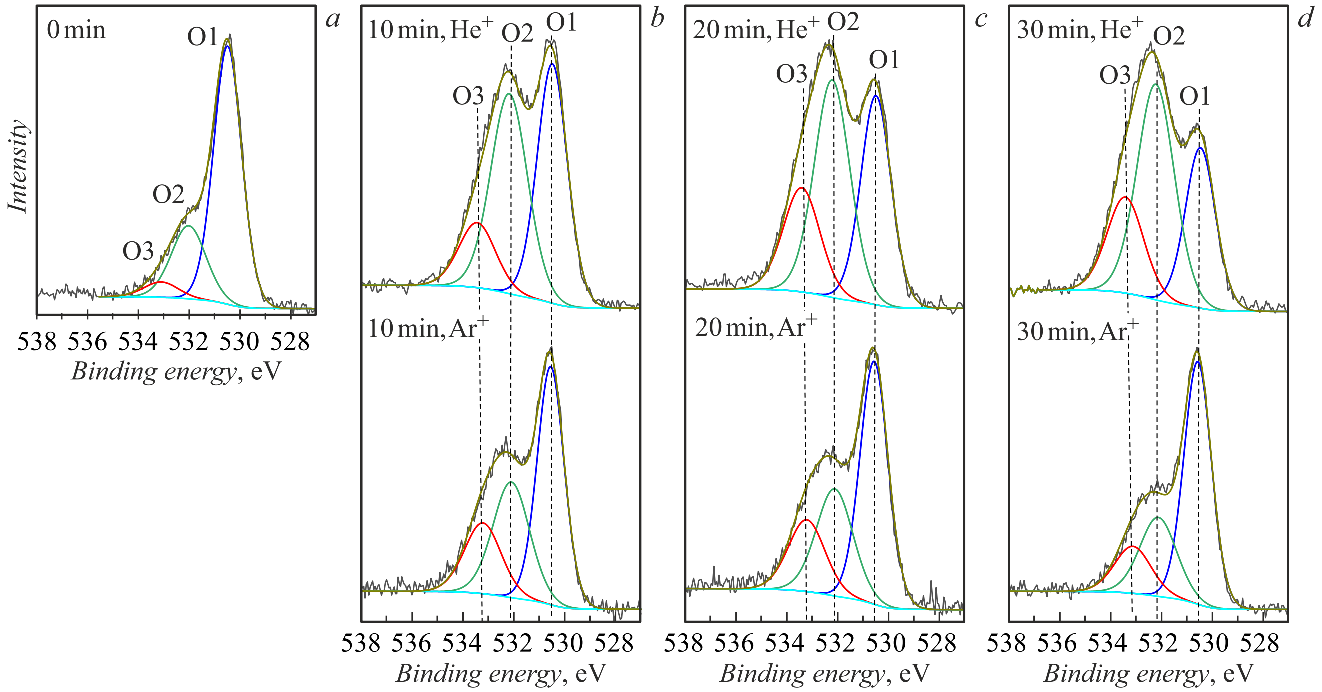

Figure 6. O 1*s* PE spectra of the surface layer of „MWCNT/Ti“ samples: before irradiation (*a*) and after 10 (*b*), 20 (*c*) and 30 min (*d*) irradiation with helium and argon ions.

changes when moving from the initial „MWCNT/Ti“ system to the irradiated systems. At the same time the maximum content of these groups is found after irradiation by helium ion beam for 20 and 30 min, and for all modes of irradiation by argon ions, which correlates with the change of values of interfacial adhesion of the MWCNT/Ti system obtained from the AFM data (Fig. 3). These results allow concluding that irradiation of „MWCNT/Ti“ with helium and argon ions at the results in the formation of chemical C–O–Ti-bonds at the interface that increase the adhesion of MWCNT to Ti. It should be emphasized that these bonds are formed with the involvement of functional C–O-groups, which are formed on the structural defects occurring in case of the ion bombardment on the MWCNTs surface. A sharp increase of the value of interfacial adhesion in the case of irradiation by argon ions for 30 min is attributable to the additional formation of direct Ti–C-bonds between MWCNTs and titanium substrate.

Conclusion

A complex study of MWCNT layers deposited on a titanium substrate showed significant changes of the morphology and chemical composition of the samples as a result of their treatment with helium and argon ions. It was found that ion irradiation of the „MWCNT/Ti“ system leads to the welding of individual nanotubes, the formation of voids during their partial destruction and, as a consequence, to a decrease in the density of the MWCNT layer, which is confirmed by SEM, EDXA, AFM, and XPS data. At the same time the increase of time of irradiation by the ion beam from 10 to 30 min result in the intensification of these processes.

The adhesive strength of MWCNTs to Ti was quantified depending on the type of ions used and the time of exposure to the ion beam. It was shown that the highest value of the adhesive strength, which is 31.8 μN, is achieved when the „MWCNT/Ti“ system is irradiated with argon ions for 10 min, which is three times higher than in the case of the untreated sample. This result is explained by the formation of C–O–Ti-bonds involving titanium and functional oxygen-containing groups on the surface of MWCNTs, which are formed near point and extended structural defects from the residual atmosphere of the ion implanter under the impact of an ion beam. In this case, a direct bonding between titanium and carbon atoms is observed only in the case of irradiation of the „MWCNT/Ti“ system with argon ions for 30 min, which, most likely, ensures an additional increase of the strength of the interfacial adhesion.

The result obtained will allow approaching the problem of improvement of the interfacial adhesion at the „MWCNTs–current-collecting substrate“ interface without using a binder, which will ensure the development of new highly efficient electrode materials based on carbon nanotubes and electrically conductive polymers for electrochemical applications (lithium-ion batteries and supercapacitors).

Acknowledgments

The equipment of the Omsk Regional Center for Collective Use of Siberian Branch of the Russian Academy of Science and the St. Petersburg State University Research Park (Centre for Physical Methods of Surface Investigation) was used in the work.

Funding

The study was performed with the support of the Russian Science Foundation grant № 21-72-10029.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov

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